Appendix E. BASS Bioaccumulation Modeling

Contents

List of Tables

ED_004888_00035758-00003

List of Figures

Overview

It is well established that fish and other aquatic biota readily bioaccumulate metals from their surrounding water, sediments, and food. Importantly, such bioaccumulated metals can represent significant toxicological threats not only to exposed aquatic organisms but also to terrestrial wildlife and humans which that consume contaminated fish or aquatic invertebrates. Consequently, as part of the Agency's integrated exposure and effects assessment of the Gold King Mine (GKM) release, EPA's BASS (Bioaccumulation and Aquatic System Simulator) model (Barber 2008a, 2012) was used to characterize the expected metal concentrations of Animas River fish under nominal background conditions and immediately before, during, and after the passage of the GKM plume which in turn could be used to assess whether Animas River fishes could be expected to bioaccumulate toxic body burdens of metals due to their exposure to the plume and whether such fish would be expected to pose a hazard to piscivorous wildlife and humans.

Approach and Methods

Model Description

BASS is a Fortran 95/2003 simulation program that predicts the population and bioaccumulation dynamics of age-structured fish assemblages that are exposed to hydrophobic organic pollutants and 1B, 2B, and borderline metals that complex with sulfhydryl groups (e.g., Cd, Cu, Hg, Pb, and Zn). The model's bioaccumulation algorithms are based on diffusion kinetics and are coupled to a process-based model for the growth of individual fish. These algorithms, which have been reviewed and compared to those used in similar models (Barber 2003, 2008b), consider both biological attributes of fishes and physico-chemical (pchem) properties of chemicals that determine diffusive exchange across gill membranes and intestinal mucosa. Important biological characteristics which are considered in BASS include the fish's gill morphometry, feeding and growth rates, and proximate composition (i.e., its fractional aqueous, lipid, and structural organic content). Similarly, important pchem properties addressed by the model include the chemical's aqueous diffusivity, n-octanol / water partition coefficient (K_{ow}), and, for metals, binding coefficients to proteins and other organic matter. BASS simulates fish growth using a standard mass balance, bioenergetic model (i.e., growth = ingestion - egestion - respiration - specific dynamic action - excretion). A fish's realized ingestion is calculated from its expected consumption rate adjusted for the availability of prey of the appropriate size and taxonomy. The community's food web is delineated by defining one or more foraging classes for each fish species based on its body weight, body length, or age. The dietary composition of each of these foraging classes is specified as a combination of benthos, incidental terrestrial insects, periphyton, phytoplankton, zooplankton, and one or more fish species. Population dynamics are generated by predatory mortalities defined by community's food web and standing stocks, physiological mortality rates, the maximum longevity of species, toxicological responses to chemical exposures, and dispersal. The model's temporal and spatial scales are that of a day and of a hectare, respectively.

BASS input data and commands are classified into four categories: simulation control parameters, chemical parameters, fish parameters, and non-fish parameters. Simulation control parameters provide information that applies to the simulation as a whole (e.g., length of the simulation, the ambient water temperature, water column depth, etc.). Chemical parameters specify the chemical's pchem properties (e.g., the chemical's molecular weight, n-octanol / water partition coefficient, metal binding coefficients, etc.) and the chemical's concentrations in various media. Fish parameters specify the fish's feeding and metabolic demands, dietary composition, predator-prey relationships, gill morphometrics, body composition, and initial conditions for the body weights, whole-body chemical concentrations, and population sizes of a fish's cohorts. Non-fish biotic parameters specify how benthos, terrestrial insects, periphyton, and plankton will be simulated.

An extensive database has been compiled for BASS in concert with its code development and applications. Using these data, an auxiliary parameterization program has been developed to estimate the bioenergetic, ecological, and morphometric parameters required by BASS using species, genus, or family-specific data. When these taxonomic levels of data are unavailable, however, this parameterization software uses inter-specific averages calculated from BASS's database supplement.

Just prior to the GKM release, the BASS parametrization software was updated to calibrate default fish parameter files (i.e., BASS *.FSH files) using species specific thermal niches as outlined by Zorn et al. (2008) and Lyons et al. (2009) and maximum specific body lengths from the PisCES (Piscine Community Estimation Software) database. The upper bounds of these thermal niches were defined to be the July mean water temperatures (JMT) of streams and rivers inhabited by the species of interest. Data sources used to construct and to assign these JMT-based niches included the WHATIF Hydrology tool (USEPA 2016), Hinz et al. (2011), Lyons et al. (2009), and Zorn et al. (2008, 2009, 2012). Additionally, the BASS parametrization software was updated to use only common and scientific names recognized by the Peterson Field Guide to Freshwater Fishes of North America North of Mexico (2011) which is based on Common and Scientific Names of Fishes from the United States, Canada, and Mexico (2004) published jointly by the American Fisheries Society and the American Society of Ichthyologists.

BASS generates the following three types of output files:

1. An output file that summarizes the user's input parameters, any input errors detected by BASS, and any warnings / errors encountered during an actual simulation.
2. An output file that tabulates selected results of the simulation. Tabulated summaries include (1) annual bioenergetic fluxes and growth statistics of individual fish by species and age class, (2) annual bioaccumulation fluxes and statistics of individual fish by species and age class, and (3) annual community fluxes and statistics of each fish species by age class.
3. A variety of CSV files that contain community state variables as well as integrated annual flow summaries and annual means for selected state variables. Users can import these files into Excel to generate their own custom analyses, plots, and/or tables.

Model Updates for the GKM Exposure Assessment

Although BASS has been successfully used to simulate MeHg [e.g., Murphy (2004), USEPA (2005), Knightes et al. (2009), Johnston et al. (2011), Reese et al. (2015), and Barber et al. (2016)], initial simulations of the GKM plume at Silverton, which had dissolved Zn concentrations at least 6 orders of magnitude greater than typical dissolved MeHg concentrations, yielded unrealistically high fish Zn concentrations. Consequently, BASS's algorithms for describing the internal distribution and excretion of metals in fish were updated to accommodate saturable kinetics.

Unlike organic chemicals that are distributed into the lipids and nonlipid organic matter (NLOM) of fish by thermodynamic partitioning, metals are distributed into the dry organic matter (DOM) of fish by binding to specific functional groups (e.g., sulfhydryl groups in the case on type 1B and 2B metals) contained within the fish's DOM. From a modeling perspective, the significance of this difference is that the concentrations of convectional organic pollutants in a fish's lipids and NLOM (i.e., C_l and C_n, respectively) can be predicted from their concentrations in the fish's whole-body water (i.e., C_a) using linear isotherms of the form

$$C_l = K_{\mathrm{LW}} C_a \qquad (.1)$$

$$C_n = K_{\mathrm{NW}} C_a \qquad (.2)$$

where K_{LW} and K_{NW} are appropriately selected partition coefficients. For example, it is generally assumed that $K_{\mathrm{LW}} = K_{\mathrm{OW}}$ and $K_{\mathrm{NW}} = K_{\mathrm{OC}}$ where K_{OW} and K_{OC} are the chemical's n-octanol / water and organic carbon-water partition coefficients, respectively. However, because the concentration of binding sites in a fish's DOM is finite, metal concentrations in the DOM of fish will approximately follow a linear isotherm only for "low" C_a and become essentially constant for "high" C_a as the metal saturates the available binding sites.

Fortunately, an empirical nonlinear isotherm for metal binding to sulfhydryl groups contained within a fish's DOM can be developed straightforwardly using the following two equations as the asymptotes of the needed isotherm:

$$C_d = C_{\mathrm{SH}} \qquad (.3)$$

$$C_d = K_{\mathrm{DW}} C_a \qquad (.4)$$

In these equations, C_d is the metal's concentration (μmol/g dry wt) in fish's DOM; C_{SH} is the sulfhydryl concentration (μmol/g dry wt) of the DOM; and K_{DW} is the metal's partition coefficient (mL/g dry wt) when sulfhydryl binding sites are non-limiting. Perhaps the most obvious class of functions which could be used for this purpose is the class of nonrectangular hyperbolas. Although hyperbolas are most commonly formulated in terms of conic cross sections, they can also be easily formulated in terms of their asymptotes (Puckle 1868). In particular, all nonrectangular hyperbolas having Equations (E.3) and (E.4) as their asymptotes can be expressed as

$$\left(C_d - C_{\mathrm{SH}}\right)\left(C_d - K_{\mathrm{DW}} C_a\right) = h \qquad (.5)$$

where h is a constant. The solutions of this quadratic equation are

$$C_d = \frac{\left(C_{\mathrm{SH}} + K_{\mathrm{DW}} C_a\right) \pm \sqrt{\left(C_{\mathrm{SH}} - K_{\mathrm{DW}} C_a\right)^2 + 4h}}{2} \qquad (.6)$$

For modeling DOM metal concentrations, the minimum root of Equation (E.6) is chosen, i.e.,

$$C_d = \frac{\left(C_{\mathrm{SH}} + K_{\mathrm{DW}} C_a\right) - \sqrt{\left(C_{\mathrm{SH}} - K_{\mathrm{DW}} C_a\right)^2 + 4h}}{2} \qquad (.7)$$

and h is assigned to be positive. Because this equation predicts that $C_d < 0$ when $C_a = 0$, it must be adjusted to ensure that $C_d = 0$ when $C_a = 0$. To accomplish this behavior, Equation (E.4) can be translated up k units, i.e.,

$$C_d = K_{\mathrm{DW}} C_a + k \qquad (.8)$$

When this modification is made, the adjusted absorption isotherm is

$$C_d = \frac{C_{\mathrm{SH}} + k + K_{\mathrm{DW}} C_a - \sqrt{\left(C_{\mathrm{SH}} - k - K_{\mathrm{DW}} C_a\right)^2 + 4h}}{2} \qquad (.9)$$

where the required translation constant is

$$k = h / C_{\mathrm{SH}} \qquad (.10)$$

Figure E-1 illustrates the behavior of Equations (E.9) and (E.10) for zinc assuming that $C_{\mathrm{SH}} = 15.3$ μmol/g dry wt [back-calculated assuming a maximum observed whole-body zinc concentration in fish is approximately 1000 ug/g dry wt; see Murphy et al. (1978) and Wiener and Giesy (1979)], $K_{\mathrm{DW}} = 17800$ ml/g dry wt [back-calculated from McGeer et al. (2003)], $h = 0.01 K_{\mathrm{DW}}$ (assumed), and the percent moisture of the fish is 75%.

Because BASS models the chemical excretion across a fish's gills and intestine based on its aqueous phase metal concentration (C_a), BASS must back-calculate a fish's C_a based on its current whole-body metal concentration C_f. To accomplish this task, BASS solves for the root of the following monotonically increasing objective function

$$z = \frac{P_a C_a + P_d C_d}{C_f} - 1 \qquad (.11)$$

where P_a and $P_d = 1 - P_a$ denote the proportions of the fish's whole body that are water and DOM, respectively. This objective function is derived directly from the following mass balance relationships

$$\begin{aligned} B_f &= W_a C_a + W_d C_d \\ \frac{B_f}{W_f} &= \frac{W_a}{W_f} C_a + \frac{W_d}{W_f} C_d \\ C_f &= P_a C_a + P_d C_d \end{aligned} \qquad (.12)$$

where B_f denotes the fish's whole-body metal burden/mass, and W_a, W_d, and W_f denote the fish's water, DOM, and whole-body masses, respectively. When Equation (E.9) is substituted in Equation (E.11), and constants terms are renamed as simple positive parameters, the required objective function can be expressed as

$$z = \frac{P_a C_a}{C_f} + \frac{P_d C_d}{C_f} - 1 \qquad (.13)$$

$$z = \frac{P_a C_a}{C_f} + \frac{P_d \left(C_{\mathrm{SH}} + k + K_{\mathrm{DW}} C_a - \sqrt{\left(C_{\mathrm{SH}} - k - K_{\mathrm{DW}} C_a\right)^2 + 4h} \right)}{2 C_f} - 1 \qquad (.14)$$

$$z = \beta_1 C_a + \beta_2 \left(\beta_3 - \sqrt{\left(\beta_4 - K_{\mathrm{DW}} C_a\right)^2 + \beta_5} \right) - 1 \qquad (.15)$$

where

$$\beta_1 = \frac{2P_a + P_d K_{\mathrm{DW}}}{2C_f} \quad (.16)$$

$$\beta_2 = \frac{P_d}{2C_f} \quad (.17)$$

$$\beta_3 = C_{\mathrm{SH}} + k \quad (.18)$$

$$\beta_4 = C_{\mathrm{SH}} - k \quad (.19)$$

$$\beta_5 = 4h \quad (.20)$$

Model Setup for the GKM Exposure Assessment

This component of the Agency's exposure assessment for the GKM release focuses on the bioaccumulation of Cd, Cu, Pb, and Zn (i.e., the dominant trace metals during the release) at the following State of Colorado sites: Silverton, Durango, and the Southern Ute Indian Tribe (SUIT) Reservation. This assessment simulated not only the bioaccumulation of Cd, Cu, Pb, and Zn immediately before, during, and after the GKM plumes at the sites of concern but also the annual background bioaccumulation of these metals for an average flow year.

To setup BASS for these for these simulations, the Agency's Animas River Team

1. Identified the species composition of fishes expected to occur at the Animas River sites impacted by the GKM release.
2. Used the BASS parameterizations software to estimate all bioenergetic, ecological, and morphometric parameters needed to simulate the growth and bioaccumulation of fishes identified in Step 1. Currently, this software provides default parameterization for 621 species of North American fishes.
3. Developed empirical distribution coefficients for calculating the concentrations of Cd, Cu, Pb, and Zn in the aqueous and DOM phases of Animas River fishes.
4. Constructed BASS exposure files for the selected Animas River sites using observed and predicted dissolved metal concentrations developed by the team's empirical fate and transport subtask.

For these assessments, all Animas River projects were executed in BASS's FGETS mode which simulates only fish growth and bioaccumulation (i.e., fish population dynamics were not simulated).

Fishes of Concern

Based on 2010 and 2012 SUIT fish surveys of the Animas River between Purple Cliffs and the New Mexico Stateline, over 97% of total fish catch were accounted for by the following species: 29.2% brown trout (*Salmo trutta*), 25.9% bluehead sucker (*Catostomus discobolus*), 18.7% rainbow trout (*Oncorhynchus mykiss)*, 12.3 % mottled sculpin (*Cottus bairdii*), 7.8 flannelmouth sucker (*Catostomus latipinnis*), and 3.3% white sucker (*Catostomus commersonii*) (Zimmerman 2013). Consequently, for this assessment, this community of fishes was assumed to be representative at each site of interest.

Because the BASS fish database is biased toward eastern and nationally distributed species, life history data concerning the growth, age/length at maturity, and time of spawning of bluehead and flannelmouth suckers were reviewed and updated in the BASS fish database for this assessment.

Estimation of Metal Distribution Coefficients K_{DW}

A straightforward method to estimate K_{DW} was developed by rewriting Equation (E.12) as follows

$$C_f = \left(P_a + P_d \frac{C_d}{C_a} \right) C_a$$
$$\frac{C_f}{C_a} = P_a + P_d K_{\mathrm{DW}} \qquad (.21)$$

Because the preceding equation converges to

$$BAF = P_a + P_d K_{\mathrm{DW}} \qquad (.22)$$

as C_a approaches steady-state with the fish's ambient environmental water concentrations (i.e., $C_a = C_w$), this equation can be used to back-calculate K_{DW} given P_a and a reasonable estimate of the steady-state BAF of the metal of concern. Published metal BAFs , however, are highly variable and inversely dependent on the environmental water concentrations used to calculate them (Chapman et al. 1996, McGeer et al. 2003, DeForest et al. 2007). Nevertheless, high fish BAFs in waters with extremely low dissolved metal concentrations and low fish BAFs in waters with extremely high dissolved metal concentrations, can both be interpreted as non steady-state phenomena that have significantly different explanations. For example, in the former case, fish are probably deriving most of their metals from foods that have already concentrated the metal of concern, and their gills function as a net excretion pathway resulting in $C_a > C_w$. In the latter case, the fish's binding sites are essentially saturated resulting not only in a nearly constant C_d / C_a but also in $C_a < C_w$. Based on these considerations, it was assumed that the mean BAFs reported by McGeer et al. (2003) could be used to back-calculate K_{DW}.

BASS Exposure Files

BASS exposure files for the GKM plumes at Silverton and Durango were constructed directly from the observed dissolved water concentrations at these sites. The water concentration of each metal before and after the plumes were arbitrarily set to the minimum of the observed water concentration immediately before and after the plumes arrived and passed. Because the plume data for the SUIT sites was much more limited than those at Silverton and Durango, for this analysis the water concentrations at this site were modeled constants equal to the medians to the available data for August 5-16, 2015.

To estimate daily background water concentrations (C_w mg/L) for an average flow year, all available dissolved metal concentrations were first fitted to the log-linear instream loading model

$$\log_{10} L = a \log_{10} Q + b \qquad (.23)$$

where Q is the site's daily discharge rate (L/s), and $L = C_w Q$ is the site's corresponding instream loading rate (mg/s). See Table E-1. Instream loading rates were then calculated for each site and metal using average daily discharges from USGS gaging stations; these loading rates and discharges were then used to generate annual time series of metal concentrations ($C_w = L / Q$) at each site. These time series, in turn, were formatted into BASS exposure files.

Readers should note that this seemingly circular method of estimating daily water concentrations was used to circumvent potential mathematic issues associated with estimating the required concentrations with the apparently more direct model

$$\log_{10} C_w = \hat{a} + \hat{b}\log_{10} Q \qquad (.24)$$

To illustrate these potential issues, we note that any time series of water concentrations and discharges can be manipulated as follows

$$\begin{aligned}
C_w &= \frac{L}{Q} \\
\log_{10} C_w &= \alpha \log_{10} L - \beta \log_{10} Q + \gamma \\
\log_{10} C_w &= \alpha \log_{10} \left(C_w Q\right) - \beta \log_{10} Q + \gamma \\
\log_{10} C_w &= \alpha \log_{10} C_w + \alpha \log_{10} Q_{10} - \beta \log Q + \gamma \\
(1-\alpha)\log_{10} C_w &= (\alpha - \beta)\log_{10} Q + \gamma \\
\log_{10} C_w &= \frac{\alpha - \beta}{1-\alpha}\log Q_{10} + \frac{\gamma}{1-\alpha} \\
\log_{10} C_w &= \hat{a} + \hat{b}\log_{10} Q
\end{aligned} \qquad (.25)$$

Since in theory, both α and β should approach 1, the lumped coefficient $\hat{b}$ could approach the indefinite form $0/0$ which could be problematic for obtaining reliable estimates either $\hat{a}$ or $\hat{b}$. Readers should also note that Equations (E.23) and (E.24) necessarily will minimize different errors and thus will yield different concentrations.

Results and Discussion

Animas Background Bioaccumulation Dynamics

Figure E-2 displays the simulated dynamics of whole-body metal concentrations (ug/g wet wt) of 2-3 year old brown trout during an average flow year at Silverton and Durango as well as the mean observed metal concentrations of fish from the Animas and San Juan Rivers (USBR 1996, Simpson and Lusk 1999, SUIT 2015) and from AK, ID, MO, and OK watersheds impacted by mining (Farag et al. 1998, Gale et al. 2004, Kiser et al. 2010, Hitselberger 2012, Allert et al. 2013, Kanouse and Brewster 2013). BASS-simulated data are displayed in red, and observed field data are displayed in blue.

Figure E-2 shows at least four notably trends. Firstly, each simulation shows a rapid initial uptake of metals during the first week of October which is a transient behavior due to assuming zero initial whole-body concentrations for all fish and metals. Secondly, with the exception of Cu at Durango and the SUIT Reservation, BASS-simulated metal concentrations of 2-3 year old trout decrease during snowmelt (i.e., early April through July). Thirdly, with the exception of Pb at Silverton, BASS-simulated metal concentrations of these trout generally decrease as the Animas River flows downstream from Silverton to the SUIT Reservation. Lastly, BASS-simulated metal concentrations at the SUIT Reservation are reasonably consistent with the mean concentrations observed for the middle and lower Animas [i.e., SUIT (2015) and USBR (1996)] which, in turn, are bounded on the low end by mean observed metal concentrations from the San Juan River (Simpson and Lusk 1999) and on the high end by mean observed concentrations from other western and Midwestern watersheds impacted by mining [i.e., Allert et al. (2013), Farag et al. (1998), Gale et al. (2004), Hitselberger (2012), Kanouse and Brewster (2013), and Kiser et al. (2010)].

Figure E-3 displays box plots for the whole-body metal concentrations (ug/g wet wt) of all age classes of all fish species during an average year at Silverton and Durango as well as box plots for all available observed metal concentrations of fish from the Animas and San Juan Rivers (USBR 1996, Simpson and Lusk 1999, SUIT 2015) and from AK, ID, MO, and OK watersheds impacted by mining (Farag et al. 1998, Gale et al. 2004, Kiser et al. 2010, Hitselberger 2012, Allert et al. 2013, Kanouse and Brewster 2013). The top and bottom of each box corresponds to the first and third quartiles of the data, respectively; the line inside the box is the data's second quartile (i.e., median); and the upper and lower bars or "whiskers" denote the data's maximum and minimum, respectively. Table E-3 summarizes the means and standard deviations (SD) of these data.

The box plots displayed in Figure E-3 show at least four notably trends. Firstly, with the exception of Pb at Silverton, BASS-simulated metal concentrations of fish decrease monotonically as the Animas River flows downstream from Silverton to the SUIT Reservation. Secondly, BASS-simulated metal concentrations at the SUIT Reservation are very consistent with those observed for the middle and lower Animas [i.e., SUIT (2015) and USBR (1996)]. Thirdly, there is a general trend for observed metal concentrations in fish from the middle and lower Animas to be noticeably higher than those observed in the San Juan River (Simpson and Lusk 1999). Lastly, BASS-simulated metal concentrations at Durango and the SUIT Reservation are reasonably consistent with those observed from other western and Midwestern watersheds impacted by mining [i.e., Allert et al. (2013), Farag et al. (1998), Gale et al. (2004), Hitselberger (2012), Kanouse and Brewster (2013), and Kiser et al. (2010)].

GKM Plume Bioaccumulation Dynamics

Figure E-4 displays the simulated dynamics of the whole-body metal concentrations (ug/g wet wt) in 2-3 year old brown trout during the GKM plumes at Silverton and Durango as well as mean observed metals of fish from the Animas and San Juan Rivers (USBR 1996, Simpson and Lusk 1999, SUIT 2015). As before, BASS-simulated data are displayed in red, and observed field data are displayed in blue.

Figure E-4 shows at least three notably findings. Firstly, with the exception of Zn at Silverton, 2-3 year old brown trout can readily uptake and excrete during and after the GKM plumes at Silverton and Durango. However, because Silverton trout are nearly saturated with respect to Zn, their uptake and excretion of Zn would be virtually undetectable. Secondly, whole-body concentrations of all metal simulated by BASS using median observed dissolved metal concentrations at the SUIT Reservation agree well with the mean observed whole-body metal concentrations for the middle and lower Animas [i.e., SUIT (2015) and USBR (1996)]. Thirdly, with the exception of Pb at Durango, all peak whole-body metal concentrations of 2-3 year old brown trout at Silverton and Durango exceeded the mean observed whole-body metal concentrations for the middle and lower Animas [i.e., SUIT (2015) and USBR (1996)].

BAF Plume and Snowmelt Dynamics

Published metal BAFs are highly variable and generally inversely dependent on the environmental water concentrations used to calculate them (Chapman et al. 1996, McGeer et al. 2003, DeForest et al. 2007). This inverse relationship can be attributed to at least three factors. The first of these is the fact that metal bioaccumulation by fish is a kinetic process. Consequently, if the ability of fish to uptake and/or to excrete metal is slower than the rate-of-change of the metal's dissolved water concentrations to which they are exposed, there necessarily must be an inverse relationship between a fish's instantaneous BAFs and its aqueous exposure concentrations. A second factor contributing to this inverse relationship, is the fact that the internal distribution of metals within fish is limited by the availability of free binding sites (e.g., sulfhydryl groups for metals like Cd, Cu, Pb, and Zn). When these binding sites approach saturation, the fish whole-body concentration approaches a constant regardless of the any further changes in their exposure concentrations. When this occurs, calculated BAFs must decrease with increasing exposure concentrations and increase with decreasing exposure concentrations. Lastly, when estimating metal BAFs across multiple sites, differences in the mean exposure concentrations across those sites will also contribute to an inverse relationship between BAFs and the associated dissolved water concentrations.

Figure E-5 displays the annual dynamics of background metal BAFs (L/kg wet wt) for all age classes of all fish species simulated by BASS during an average flow year at Silverton and Durango. Also shown in this figure are the annual dynamics of the empirically estimated dissolved water concentrations (mg/L). During much of the year, when water concentration varies relatively little, BAFs are relatively constant; see for example, Cd, Pb, and Zn at Durango from early October through start of snowmelt. However, during snowmelt, all BASS-simulated BAFs demonstrate, to a greater or lesser degree, an inverse relationship to their corresponding dissolved water concentrations. This relationship is most evident with zinc at Silverton during snowmelt. At this location and time, fish are nearly saturated with zinc, and they must excrete relatively large fraction of the whole body burdens before there is a significant decrease in their whole-body concentrations. However, because dissolved water concentrations are simultaneously decreasing, BASS-simulated Zn BAFs must increase (refer to Figure E-1).

BASS-predicted Zn BAFs at Silverton and Durango also demonstrate another dimension of the classic inverse relationship between metal BAFs and their water concentrations during the period preceding snowmelt (i.e., late December to late April). During this period, Zn BAFs at both Silverton and Durango are essential "constant" with respective to time. However, because dissolved zinc concentrations at Durango are an order of magnitude less than those at Silverton, BAFs predicted for Durango are almost an order of magnitude higher than those at Silverton.

Figure E-6 displays metal BAFs (L/kg wet wt) for all age classes of all fish species simulated by BASS during the GKM plumes at Silverton and Durango. In this figure, all BASS-predicted BAFs demonstrate strong inverse relationship with their corresponding dissolved water concentrations (C_{wd}), and Table E-4 summarizes these relationships using linear model $\log_{10} BAF = a + b\log_{10} C_{wd}$. The relative strengths of these increase relationships, compared to those predicted during snowmelt, can be attributed to the relative rates of change in dissolved water concentrations during these two events. In particular, whereas the snowmelt lasts approximately for 3 months, the GKM plumes at Silverton and Durango lasted for approximately 14 and 40 hours, respectively. Since concentration half-lives of metals in Animas River fishes vary between 3 and 16 days depending on metal and location (see Table 7-10), metal concentration in fish during the GKM plumes will generally be much further away from steady-state with their water exposures than are fish during snowmelt. Consequently, as dissolved water concentrations decrease BAFs must increase and vicea versa.

Tables

Table E-1. Summary of the regressions for estimating daily instream loadings (L μg/s) as a function of river discharge (Q L/s) using the linear model $\log_{10} L = a + b \log_{10} Q$. Data sources were the EPA STORET database and the USGS GKM database released online.

Site	Metal	a	b	r^2 adjusted	SE	n
Durango	Cd	-0.507	0.951	0.755	0.163	165
Durango	Cu	-0.771	1.29	0.619	0.304	165
Durango	Pb	0.747	0.921	0.609	0.222	165
Durango	Zn	2.11	0.881	0.542	0.244	165
Silverton	Cd	1.31	0.674	0.810	0.129	131
Silverton	Cu	2.76	0.390	0.172	0.332	131
Silverton	Pb	0.293	0.770	0.422	0.354	131
Silverton	Zn	4.21	0.588	0.838	0.102	131

Table E-2. Summary of the regressions (LLS = ordinary linear least squares regression, GM = geometric mean regression) for converting reported metal concentrations in fish fillets (C_{fl}) to whole-body concentrations (C_{wb}) using the linear model $\log_{10} C_{wb} = a + b \log_{10} C_{fl}$. Data sources are as follows: Bevelhimer et al. (1997), Gale et al. (2004), Goldstein and DeWeese (1999), Gündogdu et al. (2011), McIntosh and Bishop (1976), Mierzykowski and Carr (1998), Mierzykowski et al. (1997), NCDWR (2014), ODEQ (2003), Sjahrul (2014), and USEPA (2006, 2007).

Metal	a	b	r^2	SE	Observations	Type
Cd	-0.402	0.450	0.259	0.468	23	LLS
Cu	0.230	0.733	0.291	0.244	65	LLS
Pb	-0.072	0.642	0.465	0.556	23	LLS
Zn	0.921	0.472	0.174	0.151	95	LLS
Cd	0.505	0.883	0.448	0.395	23	GM
Cu	0.526	1.36	0.677	0.164	65	GM
Pb	0.479	0.941	0.663	0.432	23	GM
Zn	0.374	1.13	0.489	0.118	95	GM

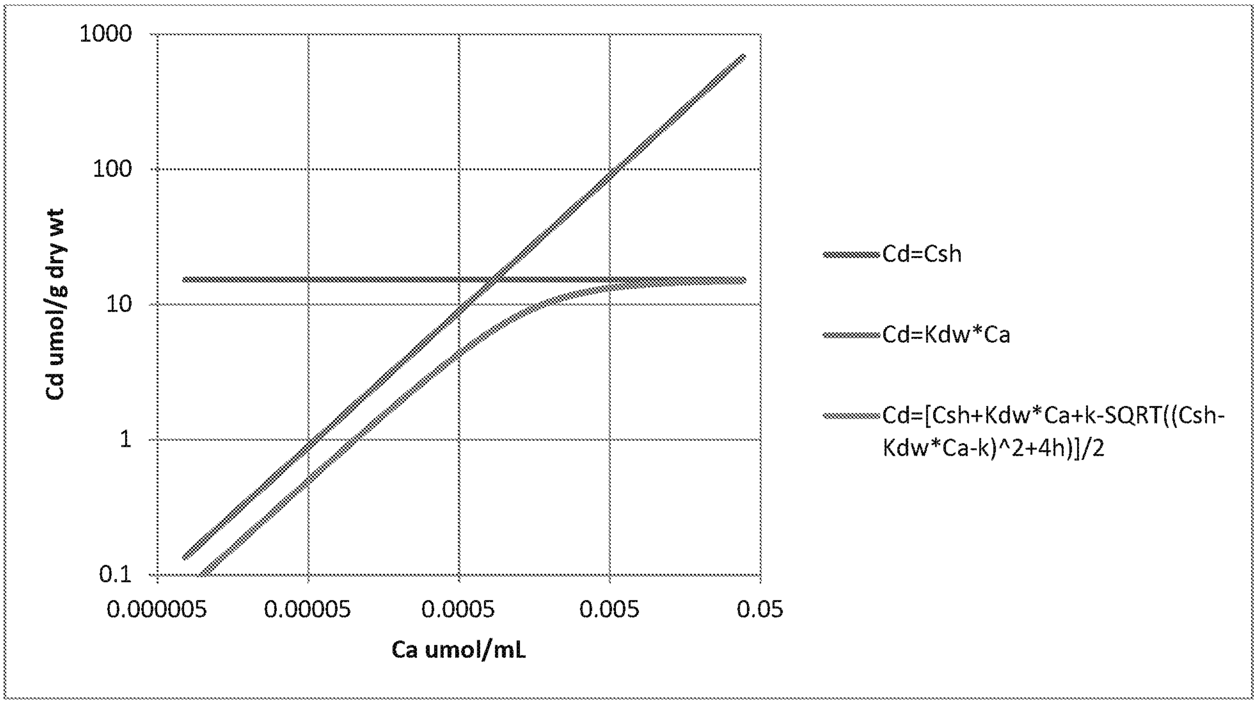
Table E-3. Means and standard deviations (in parentheses) of simulated and observed background whole-body metal concentrations (ug/g wet wt) in fish from the Animas and San Juan Rivers (USBR 1996, Simpson and Lusk 1999, SUIT 2015)and from AK, ID, MO, and OK watersheds impacted by historic or current mining. Data sources are as follows: Allert et al. (2013), Farag et al. (1998), Gale et al. (2004), Hitselberger (2012), Kanouse and Brewster (2013), Kiser et al. (2010), Simpson and Lusk (1999), SUIT (2015), and USBR (1996). Reported fillet concentrations were converted to whole-body concentrations using the geometric mean regressions summarized in Table E-2. Table abbreviations: BD = below detection; NS = not simulated; obs = observed data; sim = simulated data.

Location	type	Cd	Cu	Pb	Zn
BASS Silverton	sim	2.38 (0.740)	4.64 (2.10)	0.199 (0.050)	231 (35.4)
BASS Durango	sim	0.357 (0.056)	3.20 (0.959)	1.85 (0.293)	93.9 (15.7)
BASS SUIT	sim	0.179 (0.028)	1.60 (0.481)	0.923 (0.147)	52.7 (9.17)
Animas River (SUIT 2015)	obs	0.019 (0.002)	2.46 (2.04)	0.060 (0.061)	59.5 (28.9)
Animas River (USBR 1996)	obs	0.151 (0.064)	2.74 (1.12)	0.854 (0.931)	42.0 (20.9)
Animas River combined	obs	0.138 (0.073)	2.64 (1.48)	0.624 (0.862)	48.0 (25.0)
San Juan River (Simpson and Lusk 1999)	obs	0.047 (0.147)	2.30 (9.15)	0.261 (0.235)	28.1 (19.6)
AK,ID,MO & OK mining sites	obs	0.289 (0.294)	4.13 (9.13)	4.640 (10.6)	54.7 (32.2)

Table E-4. Summary of the regressions characterizing the relationship between the instantaneously realized $\log_{10}$ BAFs simulated by BASS and their associated dissolved water concentrations during the passage of the GKM plumes at Silverton and Durango using linear model $\log_{10} BAF = a + b \log_{10} C_{wd}$.

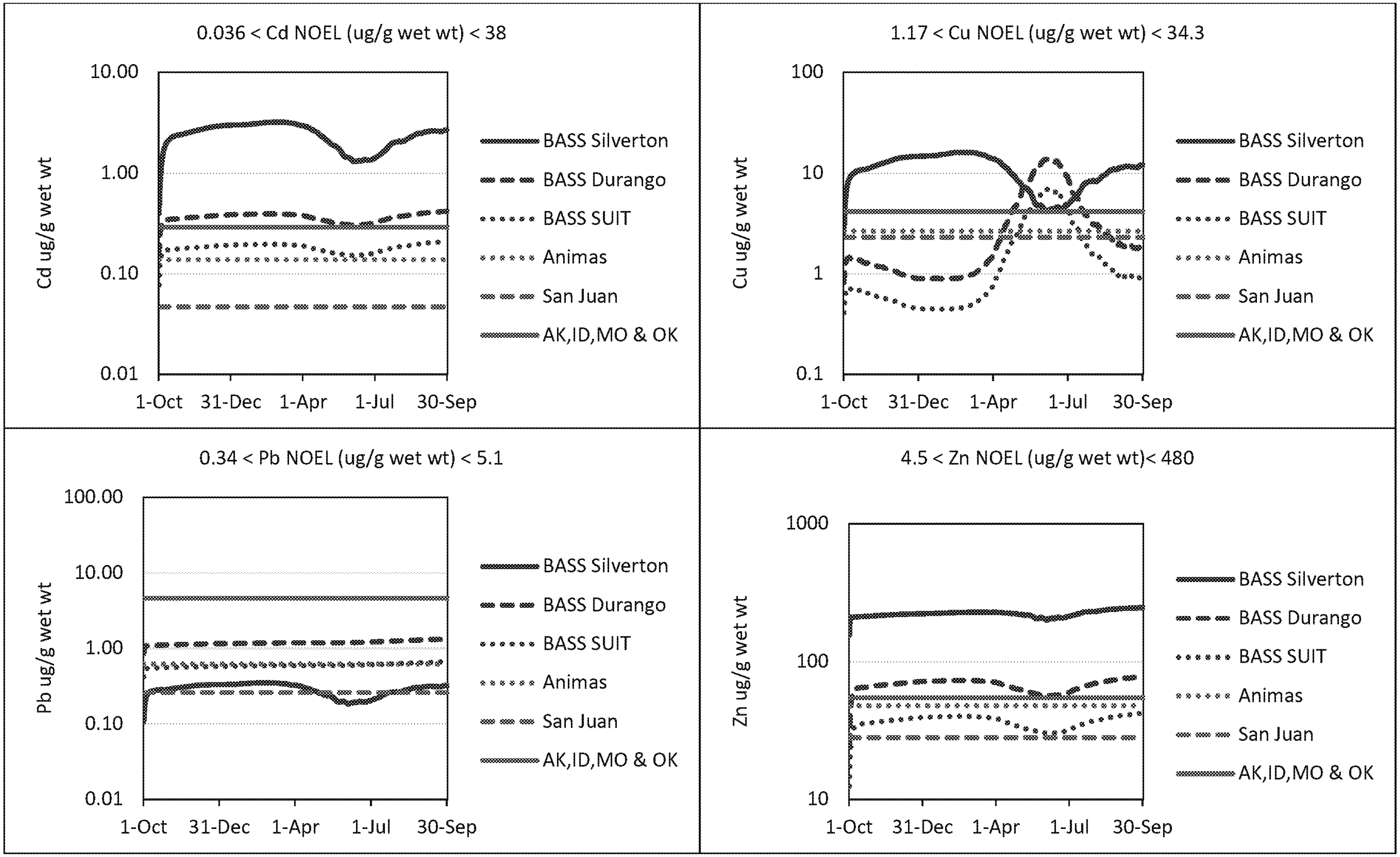
Metal	Site	a	b	r^2 adjusted	SE
Cd	Durango	-0.525	-1.02	0.928	0.103
Cd	Silverton	0.719	-1.06	0.923	0.142
Cu	Durango	0.499	-1.01	0.924	0.0709
Cu	Silverton	2.17	-0.976	0.885	0.347
Pb	Durango	-0.852	-0.984	0.773	0.221
Pb	Silverton	0.840	-1.02	0.819	0.579
Zn	Durango	1.61	-1.02	0.890	0.125
Zn	Silverton	2.39	-0.972	0.982	0.0578

Figure E-1. Plot of the hyperbolic adsorption isotherm for zinc as defined by Equations (E.9) and (E.10) where Ca and Cd denote the molar concentrations in the fish aqueous and dry organic matter, respectively.



ED_004888_00035758-00016

Figure E-2. Annual dynamics of whole-body metal concentrations (ug/g wet wt) in 2-3 year old brown trout simulated by BASS compared to field concentrations observed in the Animas and San Juan Rivers and in AK, ID, MO, and OK watersheds impacted by mining.



ED_004888_00035758-00017

Figure E-3. Box plots of annual background whole-body metal concentrations (ug/g wet wt) simulated by BASS compared to field concentrations observed in the Animas and San Juan Rivers and in AK, ID, MO, and OK watersheds impacted by mining.

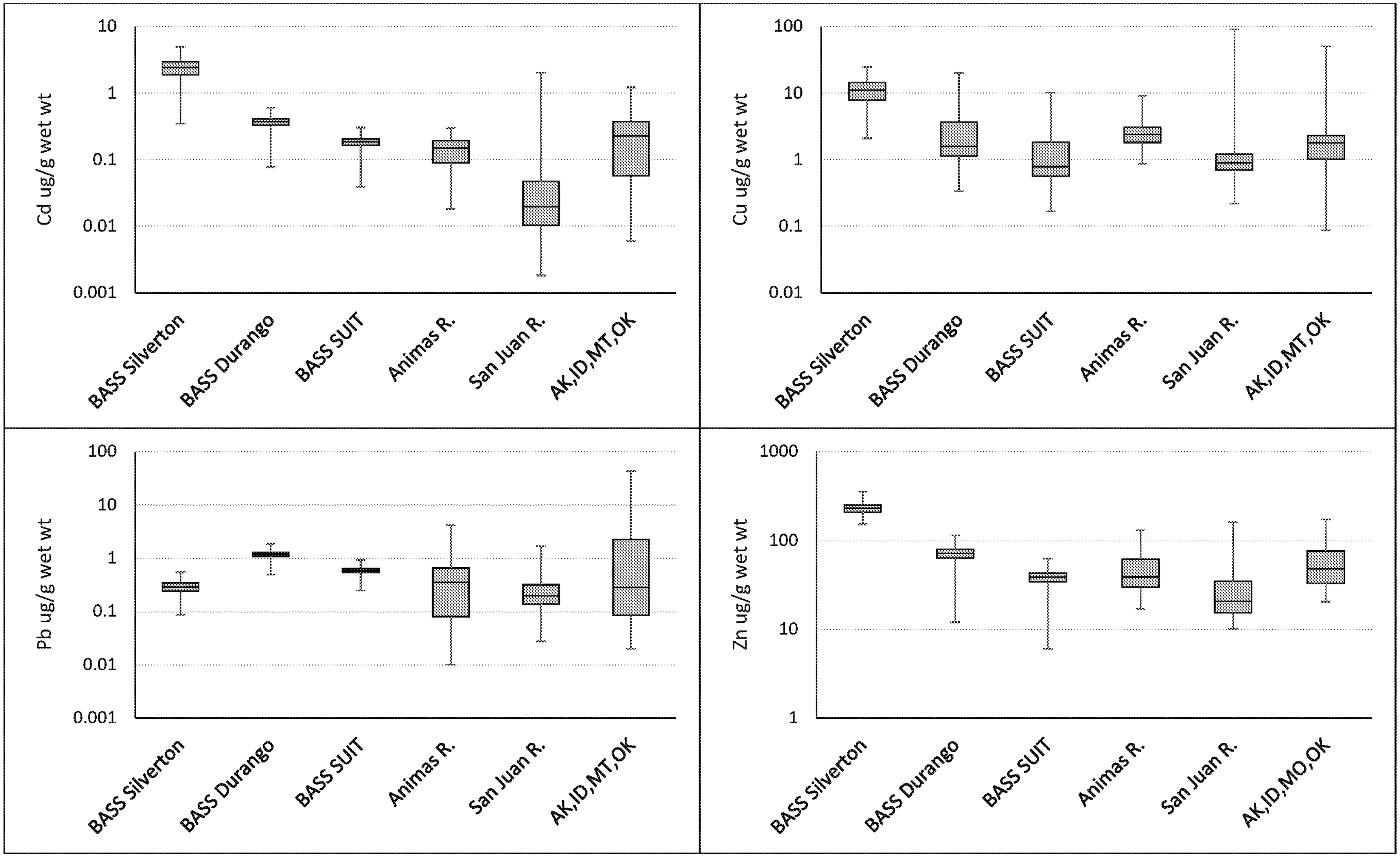


Figure E-4. Simulated dynamics of whole-body metal concentrations (ug/g wet wt) in 2-3 year old brown trout during the GKM plumes compared to field concentrations observed in the Animas and San Juan Rivers.

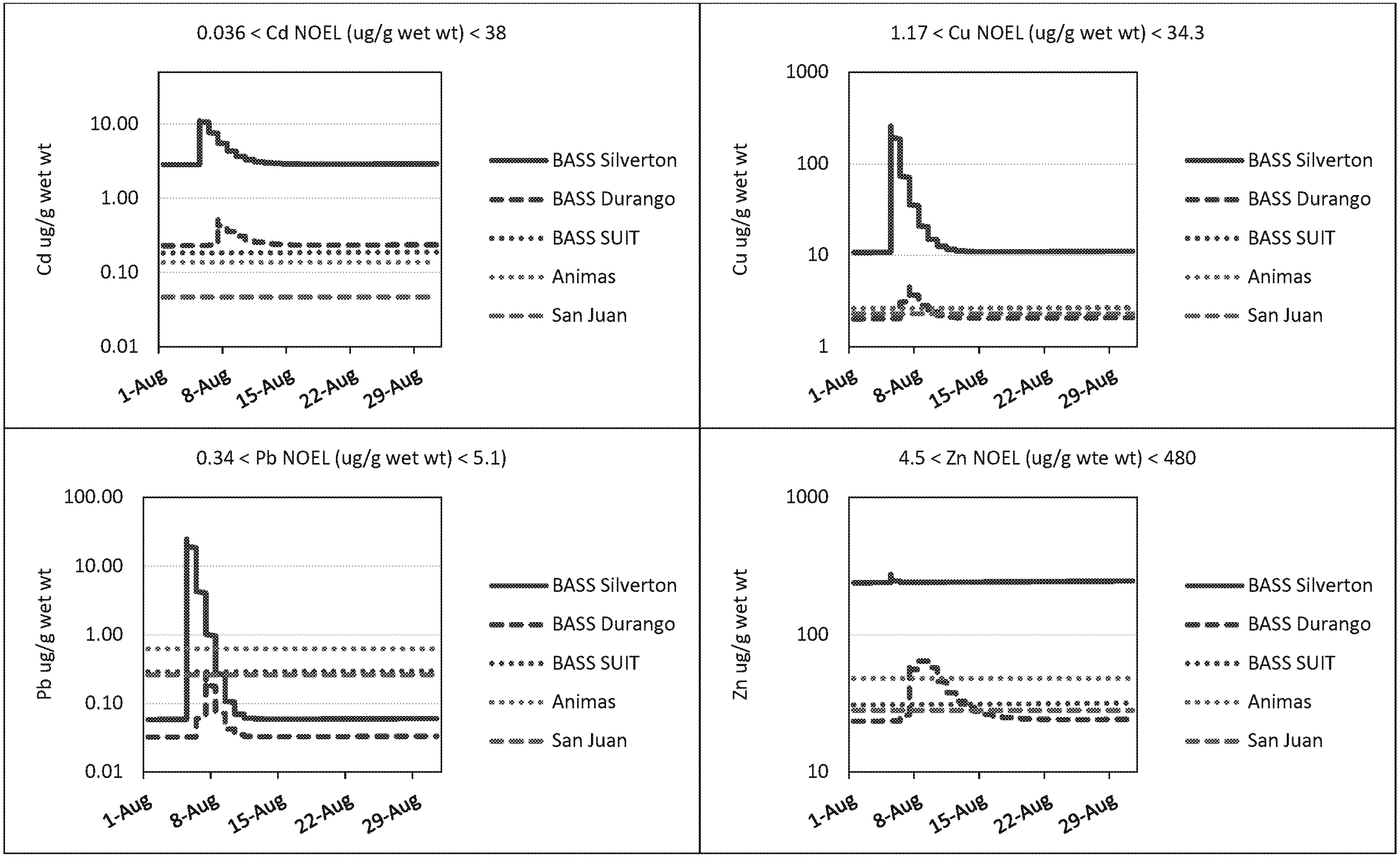


Figure E-5. Simulated dynamics of metal BAFs (L/kg wet wt) for all age classes of brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins simulated by BASS during an average flow year. Also shown are dynamics of the empirically estimated dissolved water concentrations (mg/L).

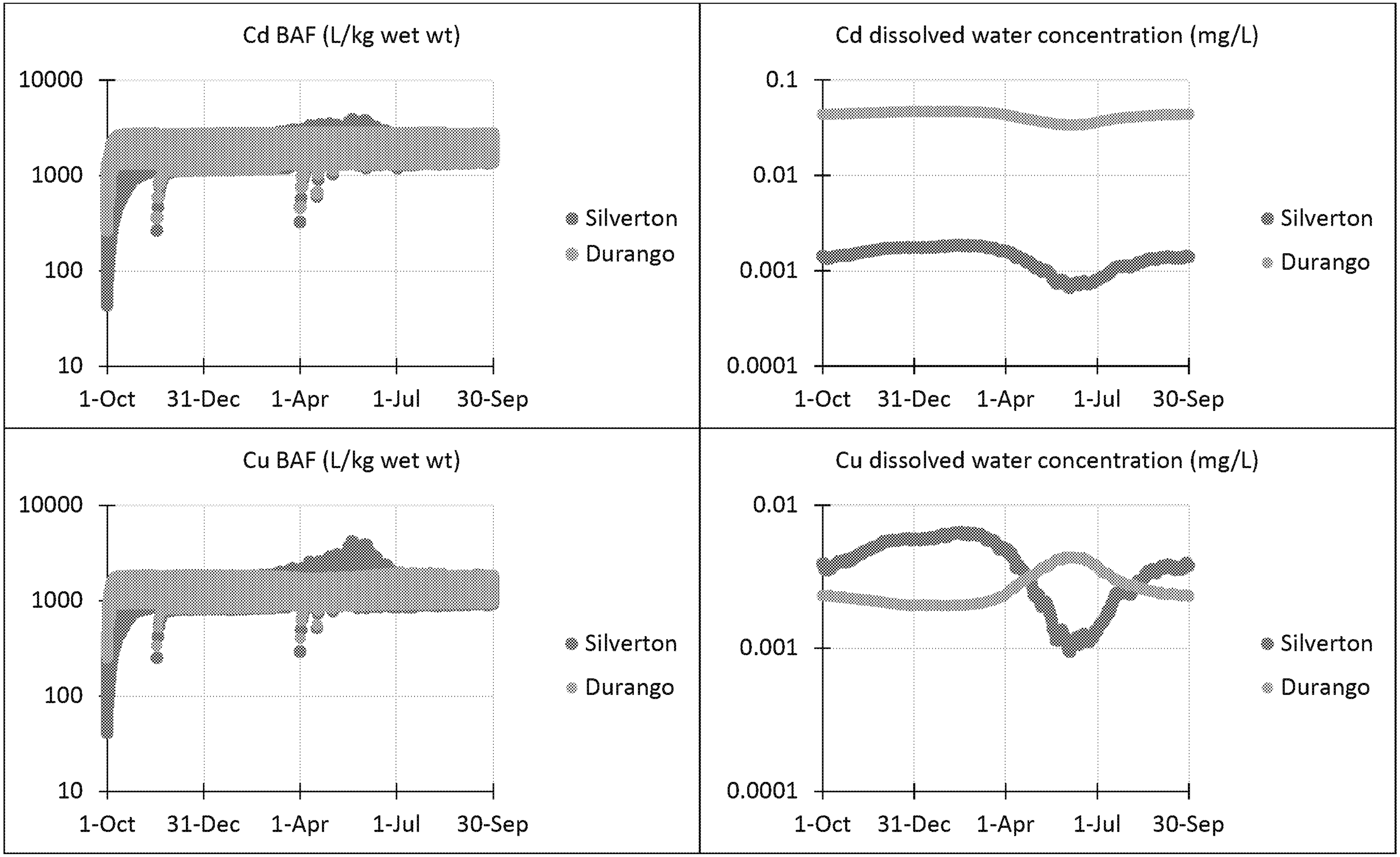


Figure E-5. Continued

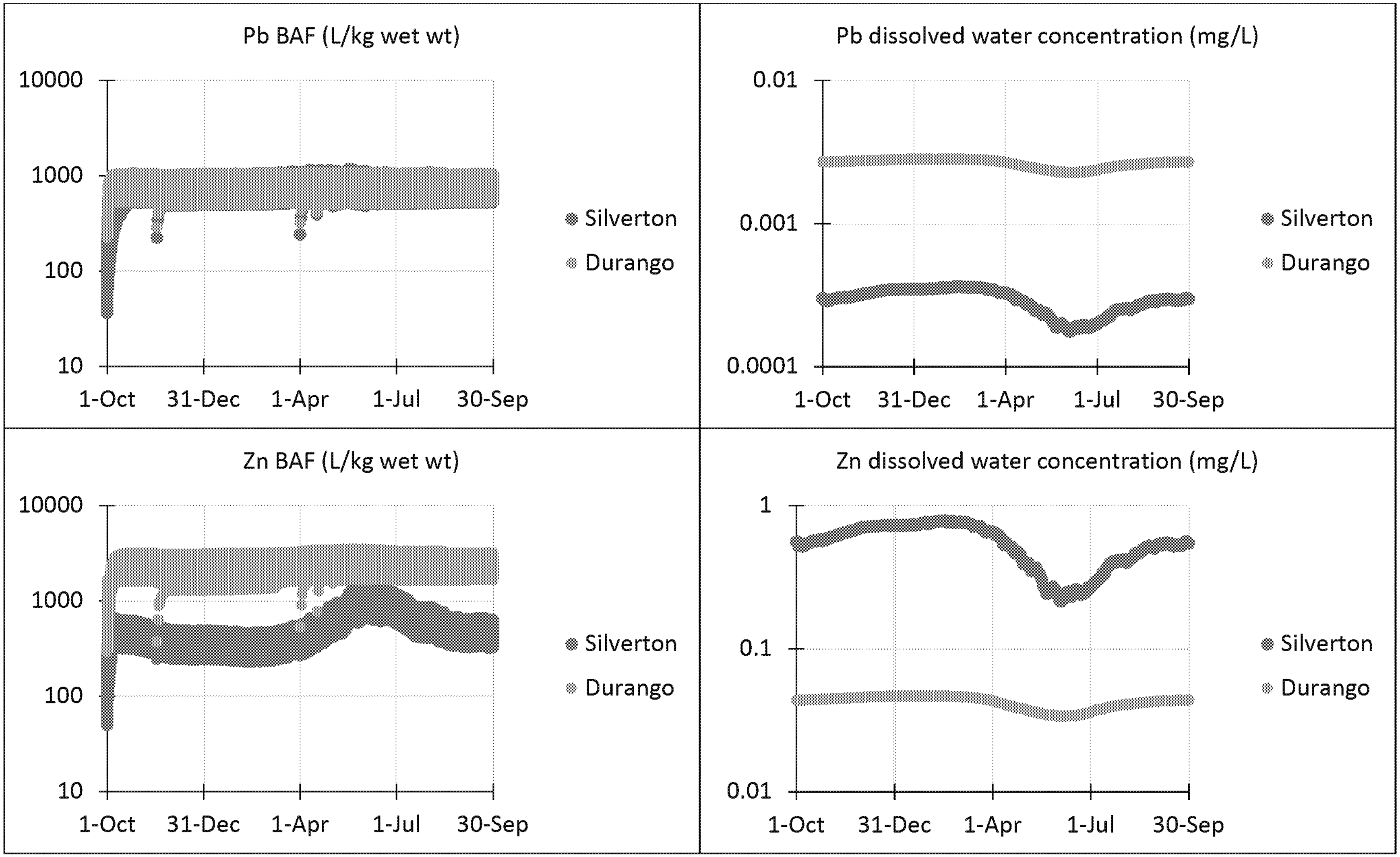
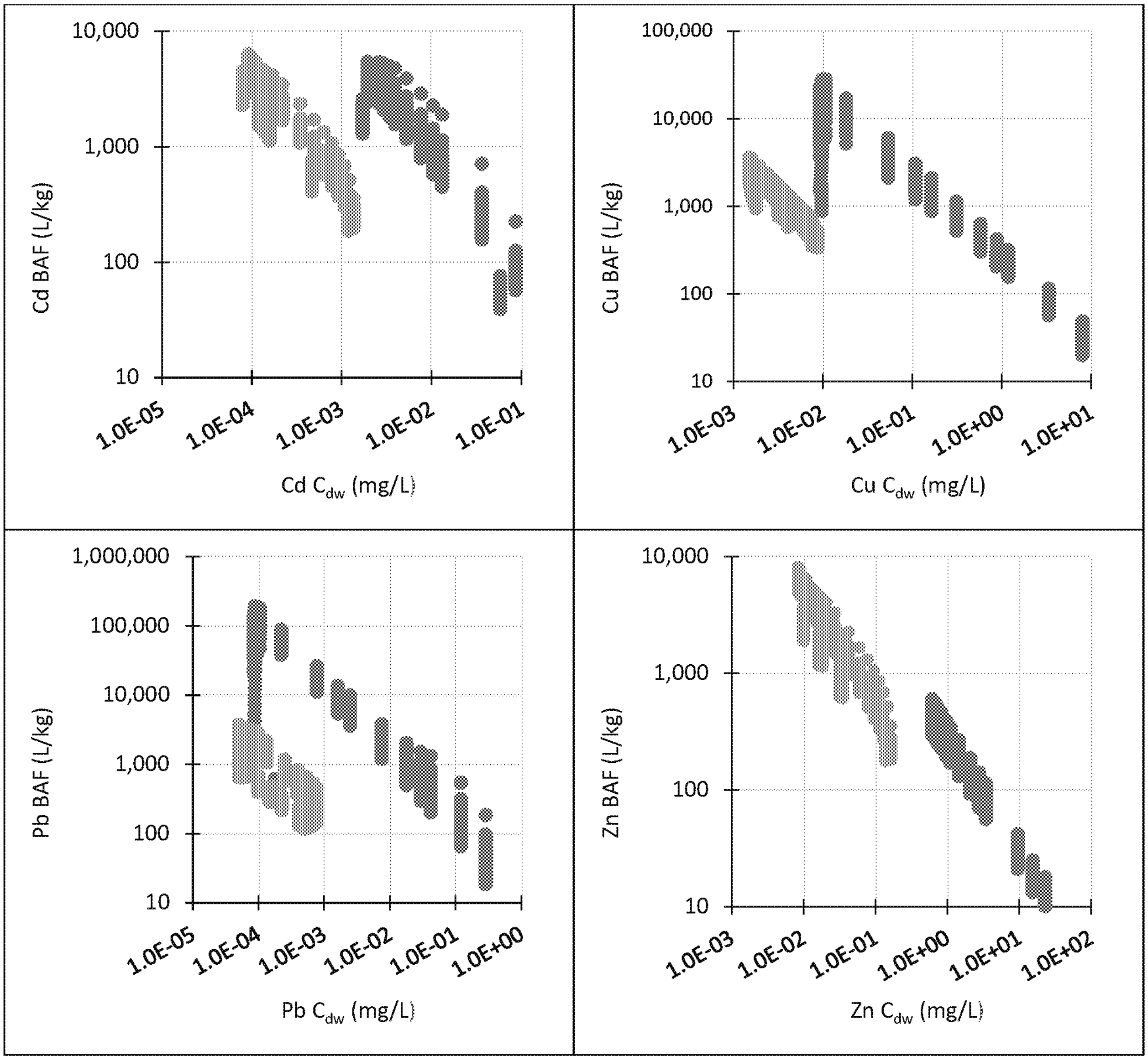


Figure E-6. BASS-predicted BAFs (L/kg wet wt) for all age classes of all fish species during the GKM plumes at Silverton (blue data, n = 2106) and Durango (orange data, n = 3128).



References

Allert, A. L., R. J. DiStefano, J. F. Fairchild, C. J. Schmitt, M. J. McKee, J. A. Girondo, W. G. Brumbaugh, and T. W. May. 2013. Effects of historical lead–zinc mining on riffle-dwelling benthic fish and crayfish in the Big River of southeastern Missouri, USA. Ecotoxicology **22**:506-521.

Barber, M. C. 2003. A review and comparison of models for predicting dynamic chemical bioconcentration in fish. Environmental Toxicology and Chemistry **22**:1963-1992.

Barber, M. C. 2008a. Bioaccumulation and Aquatic System Simulator (BASS) User's Manual Version 2.2. EPA 600/R01/035 (Update March 2008) (http://www2.epa.gov/exposure-assessment-models/bass), USEPA, Athens (GA).

Barber, M. C. 2008b. Dietary uptake models used for modeling the bioaccumulation of organic contaminants in fish. Environmental Toxicology and Chemistry **27**:755-777.

Barber, M. C. 2012. Bioaccumulation and Aquatic System Simulator (BASS) User's Manual Version 2.3. EPA 600/R01/035 (Update September 2012), USEPA, Athens (GA).

Barber, M. C., B. Rashleigh, and M. J. Cyterski. 2016. Forecasting fish biomasses, densities, productions, and bioaccumulation potentials of Mid-Atlantic wadeable streams. Integrated Environmental Assessment and Management **12**:146–159 http://dx.doi.org/110.1002/ieam.1644.

Bevelhimer, M. S., J. J. Beauchamp, B. E. Sample, and G. R. Southworth. 1997. Estimation of Whole-Fish Contaminant Concentrations from Fish Fillet Data. ES/ER/TM-202, Oak Ridge National Laboratory, Oak Ridge, TN.

Chapman, P. M., H. E. Allen, K. Godtfredsen, and M. N. Z'Graggen. 1996. Policy Analysis, Peer Reviewed: Evaluation of Bioaccumulation Factors in Regulating Metals. Environmental Science & Technology **30**:448A-452A.

DeForest, D. K., K. V. Brix, and W. J. Adams. 2007. Assessing metal bioaccumulation in aquatic environments: The inverse relationship between bioaccumulation factors, trophic transfer factors and exposure concentration. Aquatic Toxicology **84**:236-246.

Farag, M. A., F. D. Woodward, N. J. Goldstein, W. Brumbaugh, and S. J. Meyer. 1998. Concentrations of Metals Associated with Mining Waste in Sediments, Biofilm, Benthic Macroinvertebrates, and Fish from the Coeur d'Alene River Basin, Idaho. Archives of Environmental Contamination and Toxicology **34**:119-127.

Gale, N. L., C. D. Adams, B. G. Wixson, K. A. Loftin, and Y.-w. Huang. 2004. Lead, zinc, copper, and cadmium in fish and sediments from the Big River and Flat River Creek of Missouri's Old Lead Belt. Environmental Geochemistry and Health **26**:37-49.

Goldstein, R. M., and L. R. DeWeese. 1999. Comparison of trace element concentrations in tissue of common carp and implications for monitoring. JAWRA Journal of the American Water Resources Association **35**:1133-1140.

Gündogdu, A., F. B. Harmantepe, Z. Karsli, and G. Dogan. 2011. Elimination of copper in tissues and organs of rainbow trout (Oncorhynchus mykiss, Walbaum, 1792) following dietary exposure. Italian Journal of Animal Science 2011; volume 10:e1.

Hinz, L. C., Jr. , B. A. Metzke, and A. M. Holtrop. 2011. Evaluating Water Temperature, Habitat and Fish Communities in Candidate Coolwater Streams in Illinois. Prepared for Illinois Department of Natural Resources, State Wildlife Grant / Project Number (T-13-P-001). INHS Technical Report 2011 (21), 8 July 2011, Illinois Natural History Survey, Champaign, IL

Hitselberger, J. P. 2012. Tulsequah Chief Mine Acid Rock Drainage: Whole. Body Metals Concentrations in Dolly Varden Char. Technical Report No. 11-09, Alaska Department of Fish and Game, Douglas, AK.

Johnston, J. M., D. J. McGarvey, M. C. Barber, G. Laniak, J. Babendreier, R. Parmar, K. Wolfe, S. R. Kraemer, M. Cyterski, C. Knightes, B. Rashleigh, L. Suarez, and R. Ambrose. 2011. An integrated modeling framework for performing environmental assessments: Application to ecosystem services in the Albemarle-Pamlico basins (NC and VA, USA). Ecological Modelling **222**:2471-2484.

Kanouse, K. M., and B. P. Brewster. 2013. Aquatic Biomonitoring at Greens Creek Mine, 2012. Technical Report No. 12-11, Alaska Department of Fish and Game, Douglas, AK.

Kiser, T., J. Hansen, and B. Kennedy. 2010. Impacts and Pathways of Mine Contaminants to Bull Trout (Salvelinus confluentus) in an Idaho Watershed. Archives of Environmental Contamination and Toxicology **59**:301-311.

Knightes, C. D., E. M. Sunderland, M. C. Barber, J. M. Johnston, and R. B. Ambrose, Jr. 2009. Application of ecosystem scale fate and bioaccumulation models to predict fish mercury response times to changes in atmospheric deposition. Environmental Toxicology and Chemistry **28**:881–893.

Lyons, J., T. G. Zorn, J. Stewart, P. W. Seelbach, K. Wehrly, and L. Wang. 2009. Defining and characterizing coolwater streams and their fish assemblages in Michigan and Wisconsin, USA. North American Journal of Fisheries Management **29**:1130–1151.

McGeer, J. C., K. V. Brix, J. M. Skeaff, D. K. DeForest, S. I. Brigham, W. J. Adams, and A. Green. 2003. Inverse relationship between bioconcentration factor and exposure concentration for metals: Implications for hazard assessment of metals in the aquatic environment. Environmental Toxicology and Chemistry **22**:1017-1037.

McIntosh, A., and W. Bishop. 1976. Distribution And Effects Of Heavy Metals In A Contaminated Lake. Technical Report No. 85, Purdue University, Water Resources Research Center, West Lafayette, IN.

Mierzykowski, S. E., and K. C. Carr. 1998. Environmental Contaminants In Fish And Mussels From Meddybemps Lake, The Dennys River, And East Machias River Eastern Surplus Superfund Site Meddybemps, Maine. Special Project Report: FY98-MEFO-1-EC, U.S. Fish And Wildlife Service, New England Field Office.

Mierzykowski, S. E., F. T. Prior, K. L. Munney, and K. C. Carr. 1997. Environmental Contaminants In Fish From The Nashua River, Fort Devens, Ayer, Massachusetts. Special Project Report: FY97-MEFO-5-EC, U.S. Fish And Wildlife Service, New England Field Office.

Murphy, B. R., G. J. Atchison, A. W. McIntosh, and D. J. Kolar. 1978. Cadmium and zinc content of fish from an industrially contaminated lake. Journal of Fish Biology **13**:327-335.

Murphy, G. W. 2004. Uptake of Mercury and Relationship to Food Habits of Selected Fish Species in the Shenandoah River Basin, Virginia. M.S. Fisheries and Wildlife Sciences. Virginia Polytechnic Institute and State University, Blacksburg, VA.

NCDWR. 2014. NC Division Of Water Resources (NCDWR) Baseline Assessment Of Fish Tissue Metals In The Dan River Following The Eden Coal Ash Spill. North Carolina Division Of Water Resources.

ODEQ. 2003. Fish Tissue Metals Analysis in the Tri-State Mining Area FY 2003 Final Report. https://www.deq.state.ok.us/pubs/CSD/TarCreekfish.pdf, Oklahoma Department of Environmental Quality, Oklahoma City, OK.

Puckle, G. H. 1868. An Elementary Treatise on Conic Sections and Algebraic Geometry: With Numerous Examples and Hints for Their Solution, Especially Designed for the Use of Beginners. Macmillan, London and Cambridge.

Reese, B., R. G. Stahl, Jr. , R. R. Landis, C. Mancini, and S. Thakali. 2015. Site-Specific Application of the Bioaccumulation and Aquatic System Simulator (BASS) for Mercury Bioaccumulation in the South River, Virginia. SETAC North America 36th Annual Meeting, Salt Lake City, UT, 1-5 November 2015.

Simpson, Z. R., and J. D. Lusk. 1999. Environmental Contaminants In Aquatic Plants, Invertebrates, And Fishes Of The San Juan River Mainstem, 1990-1996. U. S. Fish and Wildlife Service, New Mexico Ecological Services Field Office, Environmental Contaminants Program, Albuquerque, NM.

Sjahrul, M. 2014. Studies on the level of heavy metals in the Antarctic fish. European Chemical Bulletin **3**:138-141.

SUIT. 2015. Metal Survey of Animas River Fishes. Southern Ute Indian Tribe.

USBR. 1996. Animas-La Plata Project. Colorado - New Mexico. Final Supplement To The Final Environmental Statement: Appendix B Water Quality. BR-800 493-F supapp B (3 5556 031 241821), United States Department of the Interior, Bureau of Reclamation, Washingto, DC.

USEPA. 2005. Regulatory Impact Analysis for the Clean Air Mercury Rule. EPA/452/R-05/003, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards.

USEPA. 2006. Columbia River Basin Fish Contaminant Survey 1996-1998. EPA 910-R-02-006, U.S. Environmental Protection Agency, Region 10, Seattle, WA.

USEPA. 2007. FINAL Phase I Fish Tissue Sampling Data Evaluation Upper Columbia River Site CERCLA RI/FS. . U.S. Environmental Protection Agency, Region 10 (Prepared by CH2MHILL and Ecology and Environment, Inc. CONTRACT NO 68-S7-04-01).

USEPA. 2016. WHATIF - Watershed Health Assessment Tools Investigating Fisheries. U.S. Environmental Protection Agency.

Wiener, J. G., and J. P. Giesy Jr. 1979. Concentrations of Cd, Cu, Mn, Pb, and Zn in Fishes in a Highly Organic Softwater Pond. Journal of the Fisheries Research Board of Canada **36**:270-279.

Zimmerman, B. H. 2013. 2012 Fish Studies on the Animas River Southwestern Colorado Cooperative Agreement No. R10AV40005. Southern Ute Tribe, Division of Wildlife Resource Management, Ignacio, CO.

Zorn, T. G., P. W. Seelbach, and E. S. Rutherford. 2012. A regional-scale habitat suitability model to assess the effects of flow reduction on fish assemblages in Michigan streams. Journal of the American Water Resources Association (JAWRA) **48**:871-895.

Zorn, T. G., P. W. Seelbach, E. S. Rutherford, T. C. Wills, S.-T. Cheng, and M. J. Wiley. 2008. A Regional-scale Habitat Suitability Model to Assess the Effects of Flow Reduction on Fish Assemblages in Michigan Streams. Fisheries Research Report 2089, Michigan Department of Natural Resources, Ann Arbor, MI.

Zorn, T. G., P. W. Seelbach, and M. J. Wiley. 2009. Relationships Between Habitat and Fish Density in Michigan Streams. Fisheries Research Report 2091, Michigan Department of Natural Resources, Ann Arbor, MI.

End of Appendix E